

FORM PTO-1390
(REV 10-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

FUK-85

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/890470

INTERNATIONAL APPLICATION NO.
PCT/JP00/00470INTERNATIONAL FILING DATE
January 28, 2000 ✓PRIORITY DATE CLAIMED
February 1, 1999 ✓TITLE OF INVENTION METHOD OF REMOVING CALCIUM FROM WATER CONTAINING
CALCIUM HYDROGEN CARBONATE IN HIGH CONCENTRATION


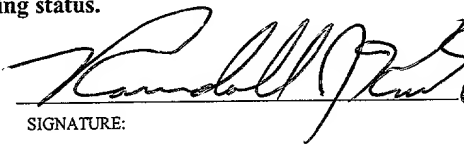
APPLICANT(S) FOR DO/EO/US Hirohisa KIKUYAMA et al. ✓

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 16 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☒ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

| | | | | | |
|---|--------------|--|------------|--|----|
| U.S. APPLICATION NO. (37 CFR 1.53) 09/890470 | | INTERNATIONAL APPLICATION NO. PCT/JP00/00470 | | ATTORNEY'S DOCKET NUMBER FUK-85 | |
| 17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT = | | | | CALCULATIONS PTO USE ONLY <div style="border: 1px solid black; height: 100px; width: 100%;"></div> | |
| | | | | \$ 860.00 | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | \$ --00-- | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | |
| Total claims | 20 - 20 = | 0 | X \$18.00 | \$ --00-- | |
| Independent claims | 1 - 3 = | 0 | X \$80.00 | \$ --00-- | |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | | + \$270.00 | \$ --00-- | |
| TOTAL OF ABOVE CALCULATIONS = | | | | \$ 860.00 | |
| <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. | | | | \$ --00-- | |
| SUBTOTAL = | | | | \$ 860.00 | |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | \$ --00-- | |
| TOTAL NATIONAL FEE = | | | | \$ 860.00 | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property | | | | \$ --00-- | |
| TOTAL FEES ENCLOSED = | | | | \$ 860.00 | |
| | | | | Amount to be | \$ |
| | | | | refunded: | \$ |
| | | | | charged: | \$ |
| a. <input checked="" type="checkbox"/> A check in the amount of \$ 860.00 to cover the above fees is enclosed. Check No. 5396 b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 501157 . A duplicate copy of this sheet is enclosed. | | | | | |
| NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status. | | | | | |
| SEND ALL CORRESPONDENCE TO: <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> CUSTOMER NO. 22855  22855 Telephone: 219-485-6001 Facsimile: 219-486-2794 </div> <div style="width: 45%; text-align: right;"> SIGNATURE:  Randall J. Knuth NAME 34,644 REGISTRATION NUMBER </div> </div> | | | | | |

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re of Applicant)
Hirohisa KIKUYAMA et al.) Art Group:
Serial No.:)
Filing Date: August 1, 2001)
Title: METHOD OF REMOVING) Examiner:
CALCIUM FROM WATER)
CONTAINING CALCIUM)
HYDROGEN CARBONATE IN)
HIGH CONCENTRATION)

PRELIMINARY AMENDMENT

Hon. Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

Applicant hereby submits the following Amendment.

IN THE SPECIFICATION

Please insert the following paragraphs into the substitute specification.

On Page 8, between lines 4 and 5 please insert the following paragraph:

--The above-mentioned and other features and advantages of this invention, and the manner of attaining them, will become more apparent and the invention will be better understood by reference to the following description of an embodiment of the invention taken in conjunction with the accompanying drawings, wherein:--

On Page 8, between lines 6 and 7 please insert the following paragraph:

--Corresponding reference characters indicate corresponding parts throughout the several views. The exemplification set out herein illustrates one preferred embodiment of the invention, in one form, and such exemplification is not to be construed as limiting the scope of the invention in any manner.--

On Page 12, line 24 please insert the following paragraph:

--While this invention has been described as having a preferred design, the present invention can be further modified within the spirit and scope of this disclosure. This application is therefore intended to cover any variations, uses, or adaptations of the invention using its general principles. Further, this application is intended to cover such departures from the present disclosure as come within known or customary practice in the art to which this invention pertains and which fall within the limits of the appended claims.--

IN THE CLAIMS

Please amend the following claims:

1. (Amended) A method for removing calcium from water containing a high concentration of calcium bicarbonate, [characterized in] comprising the steps of:

adding calcium hydroxide to waste water containing a high
5 concentration of calcium in a form of calcium bicarbonate[,
making the waste water react with calcium hydroxide,]; and
removing the calcium by fixing it to calcium carbonate.

2. (Amended) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 1, [characterized in that a] in which the
quantity of calcium hydroxide to be added ranges in 75 [-] to
5 125% of the equivalent weight to calcium.

3. (Amended) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 1, [characterized in that a] in which the
quantity of calcium hydroxide to be added ranges in 90 [-] to
5 110% of the equivalent weight to calcium.

4. (Amended) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to [any of claims 1 to 3, characterized in that said
waste water is waste water defluorinated] claim 1, further
5 comprising the step of defluorination by adding calcium carbonate
to primary waste water containing HF.

5. (Amended) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to [any of claims 1 to 4, characterized in that] claim

1, in which the water contains said calcium bicarbonate of 200ppm
or more.

6. (Amended) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to [any of claims 1 to 5, characterized in that a]
claim 1 in which said adding step comprises that the calcium
hydroxide [is to be] added [so that] causes the pH of the waste
water to range [ranges] from 8.5 to 10.5.

Please add the following new claims:

7. (New) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 2, further comprising the step of
defluorination by adding calcium carbonate to primary waste water
containing HF.

8. (New) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 3, further comprising the step of
defluorination by adding calcium carbonate to primary waste water
containing HF.

9. (New) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 2, in which the water contains said calcium
bicarbonate of 200ppm or more.

10. (New) A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 3, in which the water contains said calcium bicarbonate of 200ppm or more.

11. (New) A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 4, in which the water contains said calcium bicarbonate of 200ppm or more.

12. (New) A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 7, in which the water contains said calcium bicarbonate of 200ppm or more.

13. (New) A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 8, in which the water contains said calcium bicarbonate of 200ppm or more.

14. (New) A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 2 in which said adding step comprises that the calcium hydroxide added causes the pH of the waste water to range from 8.5 to 10.5.

15. (New) A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 3 in which said adding step comprises that the

calcium hydroxide added causes the pH of the waste water to range
5 from 8.5 to 10.5.

16. (New) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 4 in which said adding step comprises that the
calcium hydroxide added causes the pH of the waste water to range
5 from 8.5 to 10.5.

17. (New) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 5 in which said adding step comprises that the
calcium hydroxide added causes the pH of the waste water to range
5 from 8.5 to 10.5.

18. (New) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 8 in which said adding step comprises that the
calcium hydroxide added causes the pH of the waste water to range
5 from 8.5 to 10.5.

19. (New) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed
according to claim 11 in which said adding step comprises that
the calcium hydroxide added causes the pH of the waste water to
5 range from 8.5 to 10.5.

20. (New) A method for removing calcium from water
containing a high concentration of calcium bicarbonate claimed

5 according to claim 13 in which said adding step comprises that
the calcium hydroxide added causes the pH of the waste water to
range from 8.5 to 10.5.

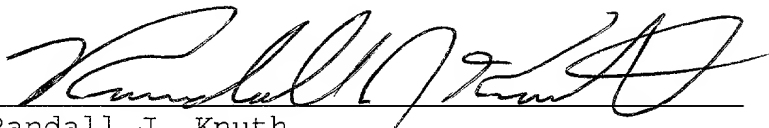
IN THE ABSTRACT

Please replace the abstract with the enclosed ABSTRACT OF
THE DISCLOSURE.

REMARKS

If the Examiner has any questions or comments that would
speed prosecution of this case, he is invited to call the
undersigned at 219/485-6001.

Respectfully submitted,


Randall J. Knuth
Registration No. 34,644

RJK/jrw

Encs: Clean Specification
Paragraphs
Clean Claims
Replacement ABSTRACT OF THE
DISCLOSURE
Return Postcard

RANDALL J. KNUTH, P.C.
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Fort Wayne, IN 46815-4631
Telephone: 219/485-6001
Facsimile: 219/486-2794

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Date of Deposit August 1, 2001.

I hereby certify that this paper or fee is being deposited with the
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Randall J. Knuth, Registration No. 34,644
(Typed Name of Person Mailing Paper or Fee)


(Signature of Person Mailing Paper or Fee)

CLEAN SPECIFICATION PARAGRAPHS

The above-mentioned and other features and advantages of this invention, and the manner of attaining them, will become more apparent and the invention will be better understood by reference to the following description of an embodiment of the invention taken in conjunction with the accompanying drawings, wherein:

Corresponding reference characters indicate corresponding parts throughout the several views. The exemplification set out herein illustrates one preferred embodiment of the invention, in one form, and such exemplification is not to be construed as limiting the scope of the invention in any manner.

While this invention has been described as having a preferred design, the present invention can be further modified within the spirit and scope of this disclosure. This application is therefore intended to cover any variations, uses, or adaptations of the invention using its general principles. Further, this application is intended to cover such departures from the present disclosure as come within known or customary practice in the art to which this invention pertains and which fall within the limits of the appended claims.

CLEAN CLAIMS

1. A method for removing calcium from water containing a high concentration of calcium bicarbonate, comprising the steps of:

adding calcium hydroxide to waste water containing a high concentration of calcium in a form of calcium bicarbonate; and
5 removing the calcium by fixing it to calcium carbonate.

2. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 1, in which the quantity of calcium hydroxide to be added ranges in 75 to 125% of the equivalent weight to calcium.

3. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 1, in which the quantity of calcium hydroxide to be added ranges in 90 to 110% of the equivalent weight to calcium.

4. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 1, further comprising the step of defluorination by adding calcium carbonate to primary waste water containing HF.

5. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 1, in which the water contains said calcium bicarbonate of 200ppm or more.

6. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 1 in which said adding step comprises that the calcium hydroxide added causes the pH of the waste water to range from 8.5 to 10.5.

7. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 2, further comprising the step of defluorination by adding calcium carbonate to primary waste water containing HF.

8. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 3, further comprising the step of defluorination by adding calcium carbonate to primary waste water containing HF.

9. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 2, in which the water contains said calcium bicarbonate of 200ppm or more.

10. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 3, in which the water contains said calcium bicarbonate of 200ppm or more.

11. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to

claim 4, in which the water contains said calcium bicarbonate of 200ppm or more.

12. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 7, in which the water contains said calcium bicarbonate of 200ppm or more.

13. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 8, in which the water contains said calcium bicarbonate of 200ppm or more.

14. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 2 in which said adding step comprises that the calcium hydroxide added causes the pH of the waste water to range from 8.5 to 10.5.

15. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 3 in which said adding step comprises that the calcium hydroxide added causes the pH of the waste water to range from 8.5 to 10.5.

16. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 4 in which said adding step comprises that the calcium

hydroxide added causes the pH of the waste water to range from
5 8.5 to 10.5.

17. A method for removing calcium from water containing a
high concentration of calcium bicarbonate claimed according to
claim 5 in which said adding step comprises that the calcium
hydroxide added causes the pH of the waste water to range from
5 8.5 to 10.5.

18. A method for removing calcium from water containing a
high concentration of calcium bicarbonate claimed according to
claim 8 in which said adding step comprises that the calcium
hydroxide added causes the pH of the waste water to range from
5 8.5 to 10.5.

19. A method for removing calcium from water containing a
high concentration of calcium bicarbonate claimed according to
claim 11 in which said adding step comprises that the calcium
hydroxide added causes the pH of the waste water to range from
5 8.5 to 10.5.

20. A method for removing calcium from water containing a
high concentration of calcium bicarbonate claimed according to
claim 13 in which said adding step comprises that the calcium
hydroxide added causes the pH of the waste water to range from
5 8.5 to 10.5.

ABSTRACT OF THE DISCLOSURE

A method for removing calcium from water containing a high concentration of calcium bicarbonate, permitting a reduction of the calcium bicarbonate equivalent to 200 - 500ppm calcium to the level in accordance with the water quality standards for industrial use, not by a method using a large amount of heat and power as heating and deairing, but by a simple chemical treatment. Calcium hydroxide is added to waste water containing a high concentration of calcium in a form of calcium bicarbonate for making them react with each other, and removing calcium by fixing it to calcium bicarbonate.

5

10

SECRET

09/890470

Hirohisa KIKUYAMA
Masayuki MIYASHITA
Toshirou FUKUDOME

METHOD OF REMOVING CALCIUM FROM WATER CONTAINING
CALCIUM HYDROGEN CARBONATE IN HIGH CONCENTRATION

BACKGROUND OF THE INVENTION

1. Field of the invention.

The present invention relates to a method for removing calcium from water containing a high concentration of calcium bicarbonate.

5 More specifically, this invention relates to a method for removing calcium from defluorinated waste water by making the waste water containing fluorine react with calcium carbonate.

10 In semiconductor device manufacturing plants, a large quantity of water such as ultrapure water or the like is used for washing, in addition to other agents such as hydrofluoric acid, ammonium fluoride. Reuse of the water by recovery and is an important problem.

2. Description of the related art.

15 Fluorinated agents consumed in a semiconductor device manufacturing plant are wasted with a large quantity of wash water.

20 In general, this waste water is processed with hydrated lime. Namely, fluoride is wasted as poorly-soluble, calcium fluoride, and water is drained out in a 15ppm or less concentration of fluorine.

Recovery of fluoride has been examined from the viewpoints of effective resource recovery and waste reduction.

In order to recover fluorine as calcium fluoride of reusable quality, a conventional process by neutralization with hydrated lime results in producing too fine particles of calcium fluoride to separate, handle, and dry them, and the process is too
5 difficult to be put into practice.

In order to obtain calcium fluoride of reusable quality, it is necessary to use calcium carbonate as a source of calcium. Calcium carbonate reacts with fluorine and is converted into calcium fluoride without change in its original shape and size. Namely, by using calcium fluoride having a 50 μm average particle
10 diameter, calcium fluoride of approximately a 50 μm average particle diameter can be obtained, and this process operates with good efficiencies in dehydration and separation.

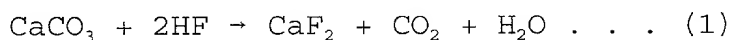
By removing fluorine by means of the above-mentioned
15 neutralization method using calcium carbonate, the fluorine in the drain can be reduced to approximately 5ppm and cleaned, treated water can be obtained.

Moreover, according to this neutralization method, calcium is removed as CaF_2 . Also, since excess calcium carbonate
20 precipitates as it is, it has been considered that Ca is not contained in the drain water after treatment.

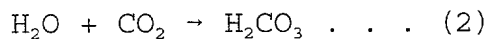
Nevertheless, through detail examinations of this treated water, it has been found out that there is quite a large amount of calcium remained in the treated water. Namely, it has been
25 found out that there is as much calcium as exceeding 75pm in

alkalinity (CaCO_3) and 120ppm in hardness (CaCO_2) specified as the water quality standards for industrial use.

For this reason, as a result of zealous search into the cause, the applicants of the present invention have considered that calcium remains therein for the following reason. Namely, carbon dioxide is by-produced by the reaction between calcium carbonate and hydrofluoric acid as shown in the following reaction formulae.



Carbon dioxide produced here is dissolved in water to produce a carbonic acid.



It is considered that calcium bicarbonate is relatively soluble, therefore, calcium remains in the drain water after treatment.

The applicants of the present invention have confirmed that after de-fluorinating waste water of about 500 - 1000ppm fluorine concentrations with calcium carbonate, it contains about 200 - 500ppm calcium dissolved therein.

Thus, water of high calcium concentration cannot be reused even as cooling water as it is, because it causes troubles such as scaling.

It is necessary to reduce its alkalinity (CaCO_3) and hardness (CaCO_2) to about 75ppm and 120ppm specified by the water quality standards for industrial use.

On the other hand, as methods for reducing the alkalinity and hardness, various methods such as classical methods as a degassing process, distillation process, an activated carbon absorption process, etc., and a ion-exchanger membrane process, dialysis membrane process, etc. have been provided.

However, it is limited from viewpoints of a life of equipment and its running costs to treat a large quantity of water of calcium concentration as high as 400 - 500ppm.

This purpose of the present invention is to provide a method for removing calcium from water containing a high concentration of calcium bicarbonate, permitting to reduce calcium bicarbonate equivalent to 200-500ppm as calcium to the level in accordance with the water quality standards for industrial use by means of a simple chemical treatment and not by means of using much heat and power for heating and deaeration.

SUMMARY OF THE INVENTION

This invention provides a method for removing calcium from water containing a high concentration of calcium bicarbonate, characterized in removing calcium by adding calcium hydroxide to waste water containing a high concentration of calcium formed as calcium bicarbonate, making the waste water react with it, and immobilizing calcium as calcium carbonate.

The applicants of the present invention have tested and examined the method for reducing the dissolved calcium bicarbonate not by using such physical methods as heating and deairing, but by using, what is called, a chemical method.

The calcium dissolved as calcium bicarbonate can be removed by converting it into a poorly-soluble calcium salt.

As poorly-soluble salts, calcium fluoride (CaF₂), calcium carbonate (CaCO₃), hydroxy-apatite (Ca₁₀(PO₄)₈(OH)₂), etc. can be mentioned.

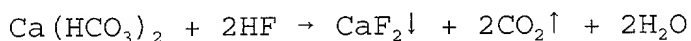
Each solubility at normal temperature is as shown in Table 1, and any of them is less than 10ppm as concentrations of Ca.

Table 1

| Kinds of Salt | Solubility | Ca concentration (ppm) |
|-------------------|---------------------------------|------------------------|
| Calcium fluoride | 0.016g/1 | 8 |
| Calcium carbonate | 0.013g/1 | 5 |
| Apatite | Ca ²⁺ 0.000123M/1 | 5 |

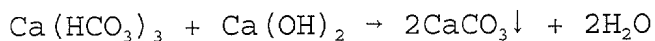
As a method for converting calcium bicarbonate dissolved in water into a poorly-soluble calcium salt, the following reactions can be mentioned, and each method has been examined.

(1) A method for removing calcium as calcium fluoride :



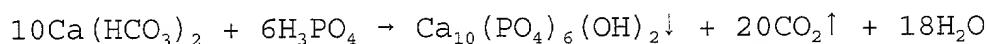
In this reaction, CaF₂ is precipitated and Ca concentration is reduced. If hydrofluoric acid is added too much, the water under treatment may be increased in F concentration. In such a case, it is necessary to remove fluorine by adding a proper quantity of calcium hydroxide.

(2) A method for removing calcium as calcium carbonate :



Calcium carbonate is precipitated by adding calcium hydroxide. In this reaction, coexisting HCO_3^{2-} is also removed as calcium carbonate at the same time, therefore, it is very reasonable for purifying the water.

5 (3) A method for removing calcium as apatite :



Hydroxy-apatite is precipitated by adding phosphoric acid, however, this reaction is considered to be conditional on a hydrogen ion concentrations (pH) or the like, and it is difficult to select the conditions, and the examinations by the applicants of the present invention did not result in almost anything like precipitation.

From the above, as a method for fixing and removing calcium dissolved as calcium bicarbonate, such a method is most reasonable, as calcium is fixed and removed as calcium carbonate having a very poor solubility by adding calcium hydroxide thereto.

This reaction does not require heating or cooling, but can sufficiently be achieved at an ordinary temperature.

20 The reaction is performed while stirring, and either one of an batch or batch system and a continuous system will do. A schematic diagram of a continuous treatment flow is shown in Fig.1.

25 Since the reaction is completed instantaneously, it is not necessary to take a long time for it but only 30 minutes are enough. In the case of the continuous system, two treating tanks

having a residence time of about 30 minutes may be cascaded for preventing a short pass.

Also in the case shown in Fig.1, a 1st treating tank 2 and a 2nd treating tank 3 are arranged in series. A waste water tank 1 is coupled to the 1st treating tank 2 via a flow controller 5. The waste water in the waste water tank 1 flows out of the bottom of the waste water tank 1, and flows into 1st treating tank from the top of it. Calcium hydroxide is added into the 1st treating tank 2 from outside. The liquid overflowing from the 1st treating tank 2 flows into the 2nd treating tank 3 from the top of it. A precipitation tank 4 is coupled downstream from the 2nd treating tank 3. The liquid overflowing from the 2nd treating tank 3 flows into the precipitation tank 4, and solid-liquid separation is performed in the precipitation tank 4. The liquid overflowing the precipitation tank 4 is supplied for reuse as supernatant liquid. Slurry containing solids precipitated in the precipitation tank 4 is forwarded to a dehydrating separator.

The treating tanks 2, 3 each are provided with respective stirrers 6,7, which stir and mix up the liquid, the waste water, to be treated, and calcium hydroxide.

The products of the reaction are separated into solids and liquid according to a conventional method. Prior to the solid-liquid separation, it is preferable to concentrate the precipitates by using the precipitation tank, a thickener, or the like. Moreover, in this case, the equipment can do with a smaller capacity by accelerating the precipitation using a small

quantity of a polymer coagulant. For solid-liquid separation, a conventional use dehydrating separator such as a centrifugal separator machine, a vacuum filter, a filter press are used.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a schematic flow diagram of a continuous treatment in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

1: Waste water tank, 2: 1st treating tank, 3: 2nd treating tank, 4: precipitation tank, 5: Flow controller, 6, 7 : Stirrer, 8: Calcium hydroxide adding equipment, and 9: pH meter.

Best Mode for Embodying the Invention :

The method of the present invention is disclosed in details by showing embodiments in the following.

(Embodiment 1)

Treated water of pH - 7 containing 4ppm F and 240ppm Ca has been obtained by making waste water containing 5000ppm HF pass through a calcium carbonate packed tower. When one liter of this treated water was sampled and a calcium reduction effect was examined varying an adding rate of calcium hydroxide, the results were obtained as shown in Table 2.

(Table 2)

| Adding rate of calcium hydroxide | pH of treated water | Concentration of Ca (ppm) | XRD of solids obtained |
|----------------------------------|---------------------|---------------------------|--|
| 50% of equivalent wt. | 7.9 | 110 | coincides with peak of CaCO ₃ |
| 75% of equivalent wt. | 8.3 | 56 | coincides with peak of CaCO ₃ |

| | | | |
|------------------------|------|----|---|
| 100% of equivalent wt. | 10.0 | 18 | coincides with peak of CaCO_3 |
| 125% of equivalent wt. | 11.1 | 66 | coincides with peak of CaCO_3 |
| 150% equivalent wt. | 11.7 | 97 | coincides with peak of CaCO_3 and a quantity of Ca(OH)_2 coexists |

The best calcium reduction effect could be obtained when an adding rate of calcium hydroxide was equivalent to the calcium concentration.

The solid obtained was calcium carbonate (CaCO_3).
(Embodiment 2)

Drain water, which was obtained by making waste water containing 5000ppm HF pass through a packed tower with a 1.5m calcium carbonate layer height and defluorinating the waste water, exhibited $\text{pH} = 7.5$, $\text{P} = 4\text{ppm}$, and $\text{Ca} = 270\text{ppm}$. From such an analysis as one liter of this drain water was sampled; 0.53 (Ca equivalent) calcium hydroxide of 95% purity was added to the water; it was treated for 30 minutes; and solid-liquid separated and analyzed, the results were obtained as shown in Table 3.

Table 3

| pH of treated water | Concentration of Ca (ppm) | Amount of solids obtained (g) | XRD of solids obtained |
|---------------------|---------------------------|-------------------------------|--|
| 9.9 | 21 | 1.20 | Coincides with peak of CaCO_3 |

(Embodiment 3)

10 liters of drain water exhibiting pH = 7.5, F = 4ppm, and Ca = 240ppm by making waste water containing 5000ppm HF pass through a packed tower with calcium carbonate of 1.5m layer height.

While making this drain water pass through the 1st tank of one liter capacity and the 2nd tank of two liters capacity arranged in series as shown in Fig.1 at a treating rate of two liters/hour, the drain water was continuously treated for 5 hours by adding 0.23g (Ca equivalent) calcium hydroxide of 95% purity into the 1st tank 2 at 30 minute intervals, and analyzed and measured by sampling the treated water overflowing from the 2nd treating tank 3 at every prescribed hours, to obtain the results as shown in Table 4.

(Table 4)

| Elapsed Time | pH | Concentration of Ca (ppm) | XRD of solids obtained |
|--------------|------|---------------------------|--|
| 2 hours | 8.9 | 22 | coincides with peak of CaCO ₃ |
| 3 hours | 10.1 | 18 | coincides with peak of CaCO ₃ |
| 4 hours | 9.8 | 23 | coincides with peak of CaCO ₃ |

Ca was stably reduced to 30ppm or smaller also by a continuous treatment system, and cleared the water quality standards.

(Embodiment 4)

Waste water containing 5000ppm HF was defluorination treated by making the water pass through a packed tower with calcium

carbonate. The analysis of the drain water exhibited pH = 6.8, F = 3ppm, and Ca = 480ppm.

After one liter of this drain water was stirred for 30 minutes by adding 1.40g calcium hydroxide of 95% purity thereto the drain water was separated into solids and liquid, then the analysis exhibited the results as shown in Table 5.

(Table 5)

| PH | F (ppm) | Ca (ppm) | XRD of solids obtained |
|------|---------|----------|--|
| 10.2 | 2 | 27 | coincides with peak of CaCO_3 |

(Embodiment 5)

Four liters of waste water treated through the calcium carbonate packed tower exhibiting pH = 6.8, F = 3ppm, and Ca = 270ppm were treated by adding calcium hydroxide thereto so as to obtain prescribed pH values, and the analysis performed according to each pH value exhibited the results as shown in Table 6.

(Table 6)

| pH | 8 | 8.5 | 9.5 | 10 | 10.5 | 11 |
|----------|-----|-----|-----|----|------|----|
| Ca (ppm) | 100 | 36 | 26 | 20 | 25 | 65 |

As shown in Table 6, it can be seen that a removal rate of Ca is significantly improved in the range of pH = 8.5 - 10.5.

(Embodiment 6)

Four liters of waste water treated through the calcium carbonate packed tower exhibiting pH = 6.8, F = 3ppm, and Ca = 270ppm were treated by adding thereto 5.4g calcium hydroxide of 96% purity so that pH value of the water becomes 10, and Table 7

shows the results of the analysis by sampling the water at each elapsed time.

(Table 7)

| | | | | | |
|---------------------|----|----|----|----|-----|
| Reaction time (min) | 5 | 15 | 30 | 60 | 120 |
| Ca (ppm) | 33 | 28 | 27 | 23 | 23 |

As shown in Table 7, the reaction is completed within a short time, and the water is sufficiently treated in 15 - 30 minutes. It can be seen from the table that the treatment is preferably carried out in 15 - 30 minutes because the effect is saturated even if it exceeds 30 minutes.

Industrial Utility:

According to the present invention, in the case of effectively recover calcium fluoride by treating fluorine containing waste water drained out of, for example, a semiconductor manufacturing plant with calcium carbonate, it is possible to reduce Ca concentration to a level to clear the water quality standards for industrial use by such a simple chemical treatment as calcium carbonate is added to waste water dissolving calcium bicarbonate with 200-500ppm calcium concentration and stirred and reacted at ordinary temperatures, and this contributes to reuse of water resource.

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METHOD OF REMOVING CALCIUM FROM WATER COUNTAINING
CALCIUMHYDROGEN CARBONATE IN HIGH CONCENTRATION

Field of the Art:

5 The present invention relates to a method for removing calcium from water containing a high concentration of calcium bicarbonate.

10 More specifically, this invention relates to a method for removing calcium from defluorinated waste water by making the waste water containing fluorine react with calcium carbonate.

15 In semiconductor device manufacturing plants, a large quantity of water such as ultrapure water or the like is used for washing in addition to the agents such as hydrofluoric acid, ammonium fluoride. Reuse of the water by recovery and is an important problem.

Background of the Art:

20 Fluorinated agents consumed in a semiconductor device manufacturing plant are wasted with a large quantity of wash water.

 In general, this waste water is processed with hydrated lime.

25 Namely, fluoride is wasted as poorly-soluble calcium fluoride, and water is drained out in a 15ppm or less concentration of fluorine.

 Recovery of fluoride has been examined from the viewpoints of effective resource recovery and waste reduction.

In order to recover fluorine as calcium fluoride of reusable quality, a conventional process by neutralization with hydrated lime results in producing too fine particles of calcium fluoride to separate, handle, and dry them, and the process is
5 too difficult to be put into practice.

In order to obtain calcium fluoride of reusable quality as one of resources, it is necessary to use calcium carbonate as a source of calcium. Calcium carbonate reacts with fluorine and is converted into calcium fluoride without change in its
10 original shape and size. Namely, by using calcium carbonate having a $50\mu\text{m}$ average particle diameter, calcium fluoride of approximately a $50\mu\text{m}$ average particle diameter can be obtained, and this process operates with good efficiencies in dehydration and separation.

15 By removing fluorine by means of the above-mentioned neutralization method using calcium carbonate, the fluorine in the drain can be reduced to approximately 5ppm and cleaned treated water can be obtained.

Moreover, according to this neutralization method,
20 calcium is removed as CaF_2 . Also, since excess calcium carbonate precipitates as it is, it has been considered that Ca is not contained in the drain water after treatment.

Nevertheless, through detail examinations of this treated water, it has been found out that there is a quite large amount
25 of calcium remained in the treated water. Namely, it has been found out that there is as much calcium as exceeding 75ppm in alkalinity (CaCO_3) and 120ppm in hardness (CaCO_3) specified as

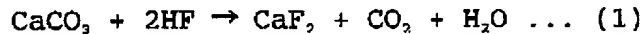
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the water quality standards for industrial use.

For this reason, as a result of zealous search into the cause, the applicants of the present invention have considered that calcium remains therein for the following reason. Namely,
5 carbon dioxide is by-produced by the reaction between calcium carbonate and hydrofluoric acid as shown in the following reaction formulae.



Carbon dioxide produced here is dissolved in water to
10 produce a carbonic acid.



It is considered that calcium bicarbonate is relatively soluble, therefore, calcium remains in the drain water after treatment.

15 The applicants of the present invention have confirmed that after de-fluorinating waste water of about 500 - 1000ppm fluorine concentrations with calcium carbonate, it contains about 200 - 500ppm calcium dissolved therein.

Thus, water of high calcium concentrations cannot be reused
20 even as cooling water as it is, because it causes troubles such as scaling.

It is necessary to reduce its alkalinity (CaCO_3) and hardness (CaCO_2) to about 75ppm and 120ppm specified by the water quality standards for industrial use.

25 On the other hand, as methods for reducing the alkalinity and hardness, various methods such classical methods as a degassing process, distillation process, an activated carbon

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absorption process, etc., and a ion-exchanger membrane process, dialysis membrane process, etc. have been provided.

However, it is limited from viewpoints of a life of equipment and its running costs to treat a large quantity of
5 water of calcium concentrations as high as 400 - 500ppm.

This purpose of the present invention is to provide a method for removing calcium from water containing a high concentration of calcium bicarbonate, permitting to reduce calcium bicarbonate equivalent to 200 - 500ppm as calcium to the level
10 in accordance with the water quality standards for industrial use by means of a simple chemical treatment and not by means of using much heat and power for heating and deaeration.

Disclosure of the Invention :

This invention provides a method for removing calcium from
15 water containing a high concentration of calcium bicarbonate, characterized in removing calcium by adding calcium hydroxide to waste water containing a high concentration of calcium formed as calcium bicarbonate, making the waste water react with it, and immobilizing calcium as calcium carbonate.

20 Actions :

The applicants of the present invention have tested and examined the method for reducing the dissolved calcium bicarbonate not by using such physical methods as heating and deairing, but by using, what is called, a chemical method.

25 The calcium dissolved as calcium bicarbonate can be removed by converting it into a poorly-soluble calcium salt.

As poorly-soluble salts, calcium fluoride (CaF_2), calcium

carbonate (CaCO_3), hydroxy-apatite ($\text{Ca}_{10}(\text{PO}_4)_8(\text{OH})_2$), etc. can be mentioned.

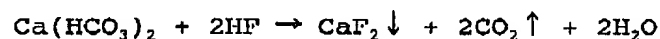
Each solubility at a normal temperature is as shown in Table 1, and any of them is less than 10ppm as concentrations of Ca.

5 Table 1

| Kinds of Salt | Solubility | Ca concentration (ppm) |
|-------------------|---------------------------------|------------------------|
| Calcium fluoride | 0.016g/l | 8 |
| Calcium carbonate | 0.013g/l | 5 |
| Apatite | Ca^{2+} 0.000123M/l | 5 |

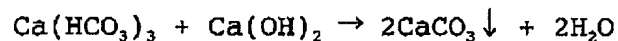
As a method for converting calcium bicarbonate dissolved in water into a poorly-soluble calcium salt, the following reactions can be mentioned, and each method has been examined.

10 (1) A method for removing calcium as calcium fluoride :



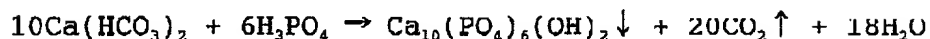
In this reaction, CaF_2 is precipitated and Ca concentration is reduced. If hydrofluoric acid is added too much, the water under treatment may be increased in F concentration. In such
15 a case, it is necessary to remove fluorine by adding a proper quantity of calcium hydroxide.

(2) A method for removing calcium as calcium carbonate :



Calcium carbonate is precipitated by adding calcium
20 hydroxide. In this reaction, coexisting HCO_3^{2-} is also removed as calcium carbonate
at the same time, therefore, it is very reasonable for purifying the water.

(3) A method for removing calcium as apatite :



Hydroxy-apatite is precipitated by adding phosphoric acid. however, this reaction is considered to be conditional on a hydrogen ion concentrations (pH) or the like, and it is difficult to select the conditions, and the examinations by the applicants of the present invention did not result in almost anything like precipitation.

From the above, as a method for fixing and removing calcium dissolved as calcium bicarbonate, such a method is most reasonable, as calcium is fixed and removed as calcium carbonate having a very poor solubility by adding calcium hydroxide thereto.

This reaction does not require heating or cooling, but can sufficiently be achieved at an ordinary temperature.

The reaction is performed while stirring, and either one of an batch system and a continuous system will do. A schematic diagram of a continuous treatment flow is shown in Fig.1.

Since the reaction is completed instantaneously, it is not necessary to take a long time for it but only 30 minutes are enough. In the case of the continuous system, two treating tanks having a residence time of about 30 minutes may be cascaded for preventing a short pass.

Also in the case shown in Fig.1, a 1st treating tank 2 and a 2nd treating tank 3 are arranged in series. A waste water tank 1 is coupled to the 1st treating tank 2 via a flow controller

5. The waste water in the waste water tank 1 flows out of the bottom of the waste water tank 1, and flows into 1st treating tank from the top of it. Calcium hydroxide is added into the 1st treating tank 2 from outside. The liquid overflowing from the 1st treating tank 2 flows into the 2nd treating tank 3 from the top of it. A precipitation tank 4 is coupled downstream from the 2nd treating tank 3. The liquid overflowing from the 2nd treating tank 3 flows into the precipitation tank 4, and solid-liquid separation is performed in the precipitation tank 4. The liquid overflowing the precipitation tank 4 is supplied for reuse as supernatant liquid. Slurry containing solids precipitated in the precipitation tank 4 is forwarded to a dehydrating separator.

The treating tanks 2, 3 each are provided with respective stirrers 6, 7, which stir and mix up the liquid, the waste water, to be treated, and calcium hydroxide.

The products of the reaction are separated into solids and liquid according to a conventional method. Prior to the solid-liquid separation, it is preferable to concentrate the precipitates by using the precipitation tank, a thickener, or the like. Moreover, in this case, the equipment can do with a smaller capacity by accelerating the precipitation using a small quantity of a polymer coagulant. For solid-liquid separation, a conventional use dehydrating separator such as a centrifugal separator machine, a vacuum filter, a filter press are used.

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Brief description of the Drawing:

Fig.1 is a schematic flow diagram of a continuous treatment in accordance with the present invention.

(Description of the Marks)

- 5 1: Waste water tank, 2: 1st treating tank, 3: 2nd treating tank, 4: precipitation tank, 5: Flow controller, 6, 7 : Stirrer, 8: Calcium hydroxide adding equipment, and 9: pH meter.

Best Mode for Embodying the Invention :

- 10 The method of the present invention is disclosed in details by showing embodiments in the following.

(Embodiment 1)

- 15 Treated water of pH = 7 containing 4ppm F and 240ppm Ca has been obtained by making waste water containing 5000ppm HF pass through a calcium carbonate packed tower. When one liter of this treated water was sampled and a calcium reduction effect was examined varying an adding rate of calcium hydroxide, the results were obtained as shown in Table 2.

(Table 2)

| Adding rate of calcium hydroxide | pH of treated water | Concentration of Ca (ppm) | XRD of solids obtained |
|----------------------------------|---------------------|---------------------------|--|
| 50% of equivalent wt. | 7.9 | 110 | coincides with peak of CaCO_3 |
| 75% of equivalent wt. | 8.3 | 56 | coincides with peak of CaCO_3 |
| 100% of equivalent wt. | 10.0 | 18 | coincides with peak of CaCO_3 |
| 125% of equivalent wt. | 11.1 | 66 | coincides with peak of CaCO_3 |

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| | | | |
|------------------------|------|----|---|
| 150% of equivalent wt. | 11.7 | 97 | coincides with peak of CaCO_3 and a quantity of Ca(OH)_2 coexists |
|------------------------|------|----|---|

The best calcium reduction effect could be obtained when an adding rate of calcium hydroxide was equivalent to the calcium concentration.

5 The solid obtained was calcium carbonate (CaCO_3).

(Embodiment 2)

Drain water, which was obtained by making waste water containing 5000ppm HF pass through a packed tower with a 1.5m calcium carbonate layer height and defluorinating the waste
 10 water, exhibited $p = 7.5$, $F = 4\text{ppm}$, and $\text{Ca} = 270\text{ppm}$. From such an analysis as one liter of this drain water was sampled; 0.53 (Ca equivalent) calcium hydroxide of 95% purity was added to the water; it was treated for 30 minutes; and solid-liquid separated and analyzed, the results were obtained as shown in

15 Table 3.

Table 3

| pH of treated water | Concentration of Ca (ppm) | Amount of solids obtained (g) | XRD of solids obtained |
|---------------------|---------------------------|-------------------------------|--|
| 9.9 | 21 | 1.20 | coincides with peak of CaCO_3 |

(Embodiment 3)

10 liters of drain water exhibiting $\text{pH} = 7.5$, $F = 4\text{ppm}$,
 20 and $\text{Ca} = 240\text{ppm}$ by making waste water containing 5000ppm HF pass

through a packed tower with calcium carbonate of 1.5 layer height.

While making this drain water pass through the 1st tank of one liter capacity and the 2nd tank of two liters capacity
5 arranged in series as shown in Fig.1 at a treating rate of two liters/hour, the drain water was continuously treated for 5 hours by adding 0.23g (Ca equivalent) calcium hydroxide of 95% purity into the 1st tank 2 at 30 minute intervals, and analyzed and measured by sampling the treated water overflowing from
10 the 2nd treating tank 3 at every prescribed hours, to obtain the results as shown in Table 4.

(Table 4)

| Elapsed time | pH | Concentration of Ca (ppm) | XRD of solids obtained |
|--------------|------|---------------------------|--|
| 2 hours | 8.9 | 22 | coincides with peak of CaCO_3 |
| 3 hours | 10.1 | 18 | coincides with peak of CaCO_3 |
| 4 hours | 9.8 | 23 | coincides with peak of CaCO_3 |

Ca was stably reduced to 30ppm or smaller also by a
15 continuous treatment system, and cleared the water quality standards.

(Embodiment 4)

Waste water containing 5000ppm HF was defluorination-treated by making the water pass through a packed tower with
20 calcium carbonate. The analysis of the drain water exhibited pH = 6.8, F = 3ppm, and Ca = 480ppm.

After one liter of this drain water was stirred for 30

minutes by adding 1.40g calcium hydroxide of 95% purity thereto, the drain water was separated into solids and liquid, then the analysis exhibited the results as shown in Table 5.

(Table 5)

| PH | F (ppm) | Ca (ppm) | XRD of solids obtained |
|------|---------|----------|--|
| 10.2 | 2 | 27 | coincides with peak of CaCO ₃ |

5

(Embodiment 5)

Four liters of waste water treated through the calcium carbonate packed tower exhibiting pH = 6.8, F = 3ppm, and Ca = 270ppm were treated by adding calcium hydroxide thereto so as to obtain prescribed pH values, and the analysis performed according to each pH value exhibited the results as shown in Table 6.

10

(Table 6)

| pH | 8 | 8.5 | 9.5 | 10 | 10.5 | 11 |
|----------|-----|-----|-----|----|------|----|
| Ca (ppm) | 100 | 36 | 26 | 20 | 25 | 65 |

15

As shown in Table 6, it can be seen that a removal rate of Ca is significantly improved in the range of pH = 8.5 - 10.5.

(Embodiment 6)

20

Four liters of waste water treated through the calcium carbonate packed tower exhibiting pH = 6.8, F = 3ppm, and Ca = 270ppm were treated by adding thereto 5.4g calcium hydroxide of 96% purity so that pH value of the water becomes 10, and Table 7 shows the results of the analysis by sampling the water at each elapsed time.

(Table 7)

| Reaction time (min) | 5 | 15 | 30 | 60 | 120 |
|---------------------|----|----|----|----|-----|
| Ca (ppm) | 33 | 28 | 27 | 23 | 23 |

As shown in Table 7, the reaction is completed within a short time, and the water is sufficiently treated in 15 - 30 minutes. It can be seen from the table that the treatment is preferably carried out in 15 - 30 minutes because the effect is saturated even if it exceeds 30 minutes.

Industrial Utility:

According to the present invention, in the case of effectively recover calcium fluoride by treating fluorine-containing waste water drained out of, for example, a semiconductor manufacturing plant with calcium carbonate, it is possible to reduce Ca concentration to a level to clear the water quality standards for industrial use by such a simple chemical treatment as calcium carbonate is added to waste water dissolving calcium bicarbonate with 200-500ppm calcium concentration and is just stirred and reacted at ordinary temperatures, and this contributes to reuse of water resource.

What is claimed are:

1. A method for removing calcium from water containing a high concentration of calcium bicarbonate, characterized in adding calcium hydroxide to waste water containing a high
5 concentration of calcium in a form of calcium bicarbonate, making the waste water react with calcium hydroxide, and removing the calcium by fixing it to calcium carbonate.

2. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to
10 claim 1, characterized in that a quantity of calcium hydroxide to be added ranges 75 - 125% of the equivalent weight to calcium.

3. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to claim 1, characterized in that a quantity of calcium hydroxide
15 to be added ranges 90 - 110% of the equivalent weight to calcium.

4. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to any of claims 1 to 3, characterized in that said waste water is waste water defluorinated by adding calcium carbonate to
20 primary waste water containing HF.

5. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to any of claims 1 to 4, characterized in that the water contains said calcium bicarbonate of 200ppm or more.

25 6. A method for removing calcium from water containing a high concentration of calcium bicarbonate claimed according to any of claims 1 to 5, characterized in that a quantity of

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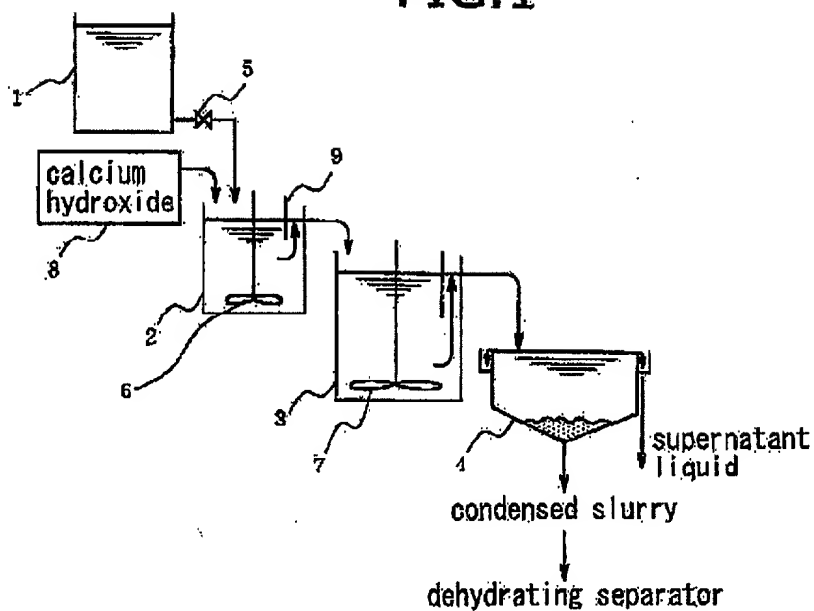
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calcium hydroxide is to be added so that pH of the waste water
ranges from 8.5 to 10.5.

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FIG.1



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ATTORNEY'S DOCKET NO. FUK-85

PCT/USA NATIONAL DECLARATION AND POWER OF ATTORNEY
FOR U.S. PATENT APPLICATIONS
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
UNDER 35 U.S.C. SECTION 371(c)(4)

As a below named inventor, we hereby declare that:

Our residence, post office address and citizenship are as stated below next to my name:

I verily believe I am the original, first and sole inventor (if only one name is listed below) or a joint inventor (if plural inventors are named below) of the invention described and claimed in international application No. PCT/JP00/00470 entitled: METHOD OF REMOVING CALCIUM FROM WATER CONTAINING CALCIUM HYDROGEN CARBONATE IN HIGH CONCENTRATION and as amended on (if any), which I have reviewed, and I understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above and for which I solicit a patent; that I do not know and do not believe that this invention was ever known or used in the United States of America before my or our invention or discovery thereof, or patented or described in any printed publication in any country before my or our invention or discovery thereof, or more than one year prior to my international application; that this invention was not in public use or on sale in the United States of America for more than one year prior to my international application; that this invention has not been patented or made the subject of an inventor's certificate issued before the date of my international application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months before my international application; that I acknowledge my duty to disclose information of which I am aware which is material to the examination of this application; and that prior to filing said international application, applications for patent or inventor's certificate on this invention or discovery which have been filed by me or my legal representatives or assigns in any country foreign to the United States of America are as follows:

(a) none filed more than 12 months prior to said international application, unless named below:

(b) earliest filed less than 12 months prior to said international application (the priority of which is hereby claimed under 35 U.S.C. Section 365):

JP 11/24444 filed February 1, 1999

I hereby claim the benefit under Title 35, United States Code, §120, of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a), which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

(Application Serial No.)

(Filing Date)

(Status)(patented, pending, abandoned)

I hereby appoint Randall J. Knuth, Regis. No. 34,644, and Vincent P. Merz, Jr., Regis. No. 45,722 of the firm of RANDALL J. KNUTH, P.C., as attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SEND CORRESPONDENCE TO:

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Hirohisa Kikuyama

Date 11. Jan. 2002.

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